

CONTRACT SPC-93-4033

First two-month Progress Report

Introduction.

Following the work performed in a previous contract (SPC-92-4003) we have continued the investigation of the electrochemical properties and of the applications of highly-conducting, gel-type polymer electrolytes. As a 'model' starting material we have selected the system formed by immobilization of liquid solutions (e.g., solutions of lithium salts in propylene carbonate-ethylene carbonate, PC/EC, mixtures) in polymer (e.g., poly(acrylonitrile), PAN) matrices. The main initial tasks of the planned work are:

i): clarify and understand the basic electrochemical properties of 'model' PAN-based, gel electrolytes (in part already achieved in the course of the previous contact);

ii) identify the most suitable applications of these electrolytes, mainly in relation to the development of lithium power sources and batteries of practical importance.

The main tasks in prospective are:

iii): identification, synthesis and test of 'new' gel-type lithium electrolytes, obtained by the replacement of the liquid solvent or of the immobilizing polymer or of both;

iv): applications of the new electrolytes.

In this initial period of the research (May.-June 1993) we have undertaken the completion of task (i) and started to develop task (ii).

Task (i)- Stability of the lithium interface.

Experimental.

The preparation of the PAN-based gel electrolytes has been described in previous reports(1). Three representative examples of PAN-based gel electrolytes have been considered, namely the systems having the following molar composition :

PAN:16/PC:23/EC:56.5/LiX: 4.5

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where the LiX salt used was LiClO_4 , LiAsF_6 and $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (high purity, reagent grade compounds), respectively. This composition gives a solvent (PC:EC mixture) to salt (LiX) molar ratio of 17.6 to 1, a value which was found to be the most suitable for assuring complete miscibility of the various components and, ultimately, a full homogeneity of the final electrolytic membranes. For simplicity reasons, the three types of electrolytes considered in this work will be thereafter indicated as:

- a) LiClO_4 - PC/EC-PAN
- b) $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -PC/EC-PAN
- c) LiAsF_6 -PC/EC-PAN

The characteristic of the lithium electrode / electrolyte interface were investigated by monitoring the evolution of the a.c. impedance of symmetrical cells of Li/PAN electrolyte /Li type, stored at room temperature under open circuit conditions for several days. Occasionally, current pulses, ranging from $25 \mu\text{Acm}^{-2}$ to 1.4mAcm^{-2} , were passed through the cell with the aim of monitoring disruption of the passivating films. The cells, having two plane, metallographic-grade polished, parallel stainless steel current collectors, were kept under constant mechanical pressure, by using calibrated spring-loaded terminals. For this investigation lithium metal (Foote Mineral Co. pure compound) was used. In order to obtain electrodes with a "clean" surface, i.e. with a surface as free as possible from native films, lithium was scraped to metallic luster in an argon-filled dry box. The impedance parameters were obtained with the same instrumentation used for the conductivity measurements. The assemblage and the test of the cells were carried out in an argon-filled dry box.

Results.

In previous reports(1) we have demonstrated that PAN-based electrolytes have a very high conductivity at ambient and subambient temperature. However, high conductivity, although an appreciable property, is not sufficient to make an electrolyte successful in practical terms. The compatibility with the electrode materials is also an essential parameter to guarantee acceptable performance in batteries, especially in terms of cyclability and reliability. Preliminary results (1) suggested that lithium electrodes may undergo passivation when in contact with PAN-based gel electrolytes. To further investigate this crucial aspect and with the attempt of determining the stability of

the lithium interface under prolonged time scale, we have carried out a detailed impedance analysis of symmetrical cells of the Li/electrolyte/Li type, stored under different conditions.

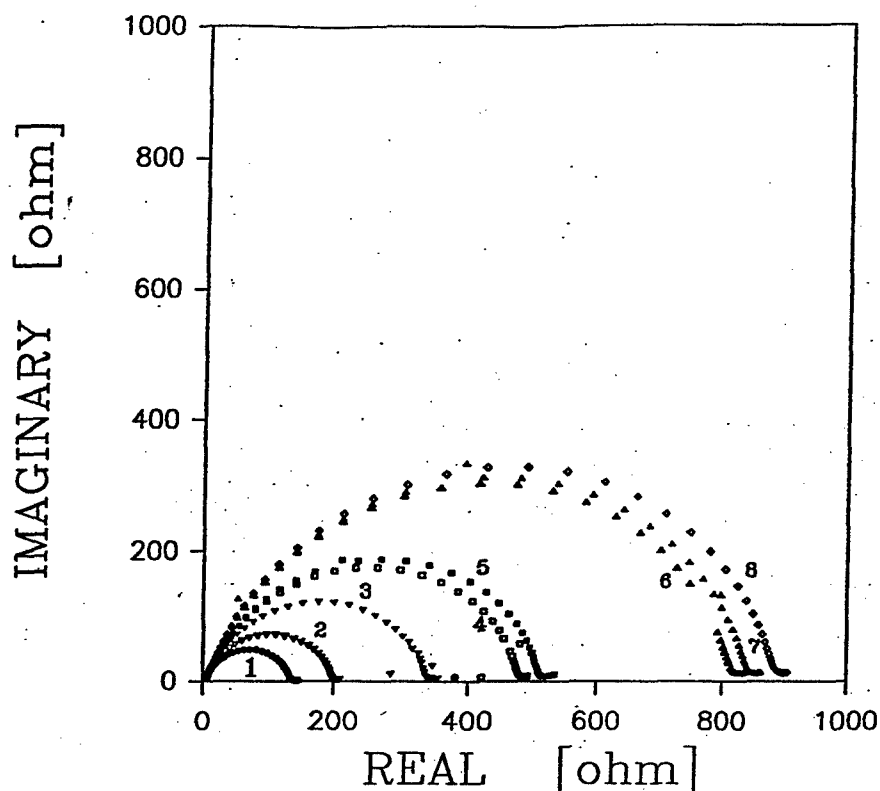


Figure 1- Time evolution of the impedance response of a symmetrical Li / LiClO₄ - PC/EC-PAN / Li cell at 25 °C and under different storage conditions.

1) after assemblage; 2) after 3 hours storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 33 minutes; 3) after 21 hours storage in OCV; 4) after 45 hours storage in OCV; 5) after 48 hours storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 66 minutes; 6) after 111 hours storage in OCV; 7) after 113 hours storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 66 minutes; 8) after 115 hours storage in OCV.

Figure 1 illustrates the time evolution of a cell using the LiClO₄ - PC/EC-PAN electrolyte. In this particular test the cell was mostly maintained in open circuit conditions, with occasional perturbations induced by short potentiostatic pulses carried out with the intent of determining the effects of the passage of current on the interface conditions (e.g. clearing, film disruption, and so forth). The $-jZ''$ - Z' plots clearly reveal a progressive expansion of the middle frequency semicircle and that the short

current pulses do not seem to produce any sensible effect in controlling this tendency. The expansion of the semicircle may be associated with a continuous growth of a resistive layer on the lithium electrode surface, which in turn indicates that this electrode is passivated when in contact with the PAN gel electrolyte. This behavior is not surprising since some of the electrolyte components (i.e., EC and, particularly, PC) are well known lithium corrosive agents. As discussed in the previous reports(1), these compounds spontaneously evaporate from the bulk of the gel electrolyte and therefore, it is reasonable to assume that the solvents, and PC in particular, continuously reach the lithium interface inducing the observed passivation effects. The trend of Figure 1 suggest that these effects induce a quite uniform resistive layer on the lithium electrode surface which cannot be easily disrupted by modest current flow

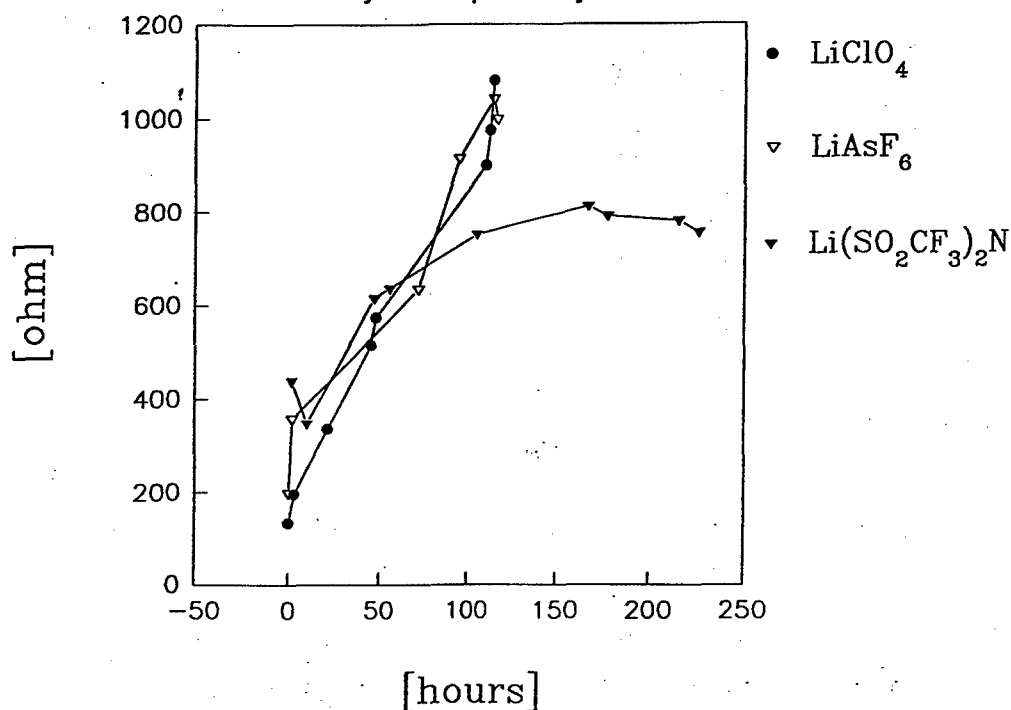


Figure 2- Time evolution of the interfacial resistance of the lithium electrode in the LiClO₄ - PC/EC-PAN, LiAsF₆ -PC/EC-PAN and LiN(CF₃SO₂)₂ -PC/EC-PAN gel electrolytes under the conditions illustrated in Figures 1, 3 and 4.

By using a model circuit which may represent the electrical equivalent of the lithium interface(1), it is possible to separate the various impedance parameters which contribute to determine the response illustrated by Figure 1. In this way one may obtain the time evolution of the lithium interfacial resistance

as reported in Figure 2: the trend for the LiClO_4 -based electrolyte cells confirms the occurrence of a continuous growth of the resistive layer with a progressive and cumulative effect.

The time evolution of the impedance response of symmetrical lithium cells using the second type (b) of the electrolytes considered in our work, namely of cells of the $\text{Li}/\text{Li}(\text{CF}_3\text{SO}_2)_2\text{-PC/EC-PAN/Li}$ type, is illustrated in Figure 3. Also in this case the middle frequency semicircle expands, this again indicating the occurrence of lithium passivation phenomena. However, some difference both at the initial and at the final stage of the test may be noted here in respect to the previous case. First, at the initial stage the polarization pulse is still capable of reducing the expansion of the semicircle, this indicating that the growth of the layer can be effectively .

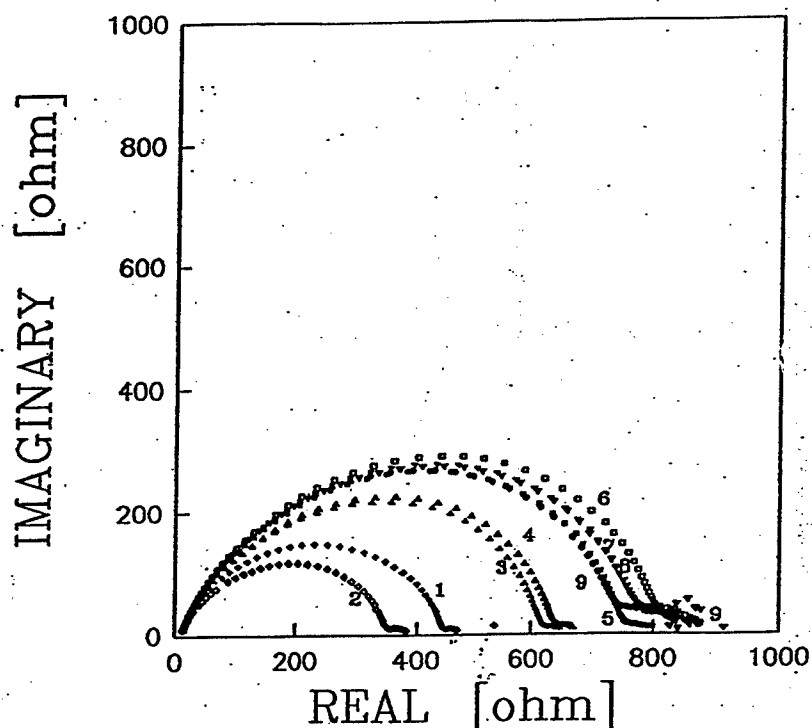


Figure 3- Time evolution of the impedance response of a symmetrical $\text{Li}/\text{Li}(\text{CF}_3\text{SO}_2)_2\text{-PC/EC-PAN/Li}$ cell at $25\text{ }^\circ\text{C}$ and under different storage conditions.

1) after 1.5 hours in OCV; 2) after 10 hours storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 480 minutes; 3) after 47 hours storage in OCV; 4) after 55 hours storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 480 minutes; 5) after 105 hours storage in OCV; 6) after 167 hours storage in OCV; 7) after 177 hours storage in OCV; 8) after 226 hours storage in OCV.

controlled by current flow through the interface. Then, we notice that the extent of the expansion progressively decreases upon storage, this suggesting that the passivation tends to reach a final level with no further progression. These aspects are confirmed by the trend of the interfacial resistance evolution reported in Figure 2

Finally, the time evolution of the impedance response of the third case, namely of a symmetrical Li / LiAsF₆ -PC/EC-PAN / Li cell, is shown in Figure 4. The response is qualitatively similar to that of the previously discussed cells. However, the comparison of the trend of the interfacial resistance (Figure 2) reveals that the kinetics of passivation are specifically different, being slow at the initial stage to then becoming progressively much faster.

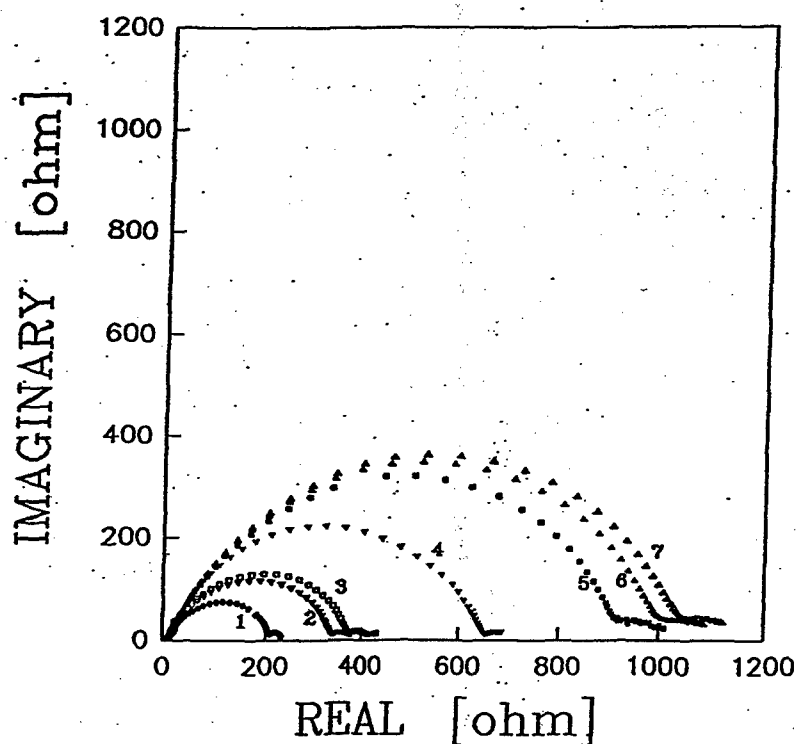


Figure 4- Time evolution of the impedance response of a symmetrical Li / LiAsF₆ -PC/EC-PAN / Li cell at 25 °C and under different storage conditions.

1) after assemblage; 2) after 1 hour storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 0.7 minutes; 3) after 72 hours storage in OCV; 4) after 95 hours storage in OCV; 5) after 115 hours storage in OCV; 6) after 117 hours storage in OCV followed by a d.c. voltage (10 mV) polarization pulse for 30 minutes.

Conclusions.

The impedance analysis here reported indicates that the passivation of the lithium electrode takes place in all the three electrolytes examined, although with a different growth kinetics. This poses some questions on the type of applications to which these electrolytes can be effectively directed. In fact, the results here discussed suggest that the PAN-based electrolytes, and quite likely the majority of the wet polymer electrolytes which generally contain aggressive liquid components, do not fulfill the requirements for being used as separators for long-life, rechargeable lithium metal batteries. Therefore, if one wants to successfully exploit the outstanding conductivity advantages of these electrolytes, configurations either for primary batteries or for electrochemical systems where any contact with the lithium metal is avoided, should be considered. Therefore, in this project, we will continue to investigate the properties of the gel electrolytes in relation to the above preferred applications..

Task (ii)- Applications of PAN-based gel electrolytes. **Primary lithium batteries.**

Introduction.

We report some preliminary results on an improved, thin-layer, new solid-state lithium battery having unique characteristics in terms of high and constant discharge voltage and of reliability. We believe that these characteristics make the battery of importance for the electronics market, both in the advanced consumer range (e.g., smart credit cards, computers, etc) and, in particular, in the military range (e.g., instrumentation and memory back-up).

The novelty of this battery is that of using new-concept, low-resistance cathode materials in connection with the highly conductive, PAN-based gel electrolytes. This combination gives very flat (constant voltage) discharge curves and high-performance operation at ambient and subambient temperatures. A detailed description of the battery structure, of its performance and expected impact in the electronic market, has been sent to Dr. R.Marsh at WL/POOS for patent consideration.

Experimental.

The battery is fabricated in a laminated structure which includes the sequence of a lithium metal anode strip (optimized thickness: 30 μm), a polymer electrolyte film (typical thickness: 100 μm) and a composite cathodic membrane (typical thickness: 400 μm). One possible battery geometry is illustrated in Figure 5.

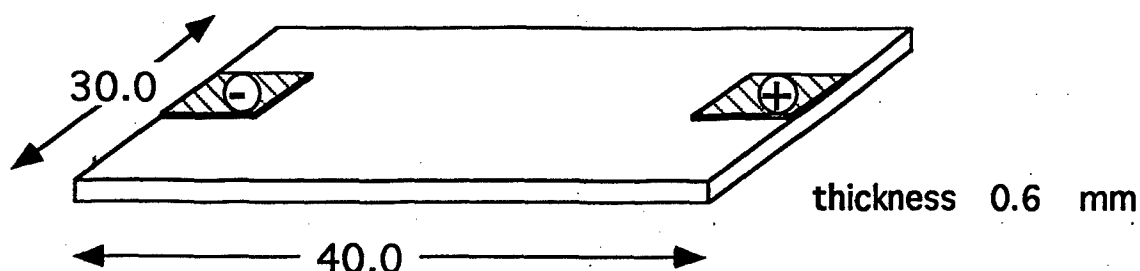


Figure 5 - Schematic of the thin-film battery configuration.

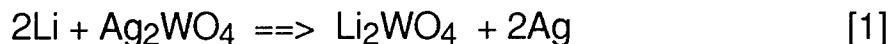
In this report we describe results obtained with the electrolyte of type (a), namely the LiClO_4 /PC/EC-PAN. electrolyte. However, we believe that also the other two types, as well as generally any other lithium salt solutions-polymer systems, capable of assuring similar conductivity and stability, can be used in alternative.

The cathodic membrane is formed by blending a mixture of carbon black and the electrochemically active compound (Ag_2WO_4) with poly(vinyl chloride) PVC. The active compound provides the battery capacity, while the carbon and the polymer additives confer the electronic conductivity and the plasticity, respectively, to the whole cathodic membrane. In this report we describe results obtained using Ag_2WO_4 as the example active compound. However, we believe that other silver (e.g., molybdate, chromate, etc) and other metal (e.g., copper, iron,) salts can be used in alternative. In this preliminary study we have used the following cathode composition (in weight ratio): Ag_2WO_4 =: 75%, C=5% and PVC=20%

Results.

The proposed electrochemical system, i.e. the $\text{Li-Ag}_2\text{WO}_4$ system, has been exploited some years ago in our laboratory in liquid electrolyte batteries (2,3) but, to our knowledge, it has never been used in the case of solid-state, lithium polymer batteries. Therefore,

the battery here proposed has some interesting and innovative features. The main (first step) discharge process:



is **not an intercalation** reaction (as it is the common case for the lithium polymer batteries today under development) but rather a **displacement** reaction, producing the Li_2WO_4 compound and the metal Ag. This in turn gives some very relevant advantages. First, being based on a two-phase process, the discharge voltage remains fixed until completion of the electrochemical balance (namely, to the consumption of two Li equivalents for M_2YO_4 mole). Second, and perhaps more important, the continuous production of the finely dispersed silver metal assures a good electronic contact throughout the entire cathodic mass and this consistently reduces ohmic polarization during discharge.

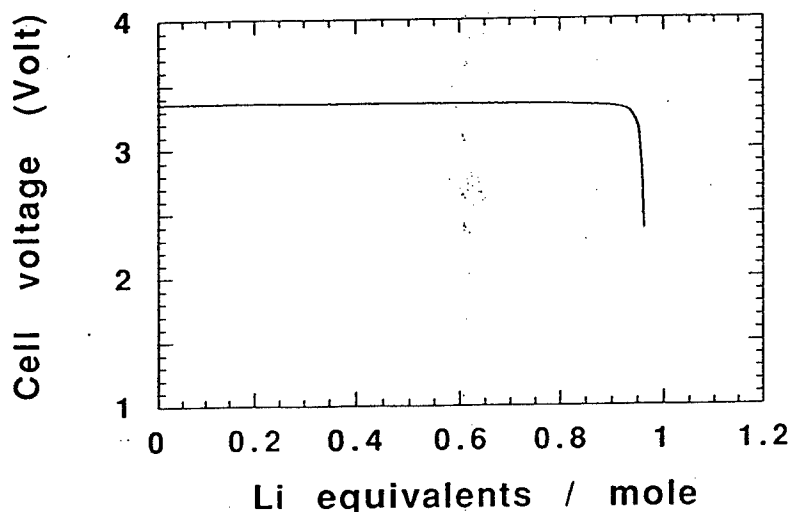


Figure 6- Typical (1st step) discharge curve of the $\text{Li}/\text{Ag}_2\text{WO}_4$ thin-film, polymer battery at room temperature and at $10 \mu\text{Acm}^{-2}$ current density. Electrolyte: $\text{LiClO}_4/\text{PC}/\text{EC}-\text{PAN}$.

This is clearly shown by Figure 6 which illustrates a typical discharge curve run at $10 \mu\text{Acm}^{-1}$, namely at a rate usually required for most of microelectronic devices. One can easily see the exceptional flatness of the curve, which remains constant around 3.3V for the entire discharge. This is an unique and very appealing feature. In fact, a

constant voltage discharge is an ideal characteristic for power sources designed for the electronic market and the occurrence of an extra step which can adsorb incidental overdischarge and short circuiting, improves consistently the battery safety and reliability. Furthermore, the control of the ohmic drop gives expectations of high rate capabilities. Indeed, one can notice from Figure 7 that the battery can sustain very high current pulses still maintaining its unique characteristics in terms of high and constant voltage values.

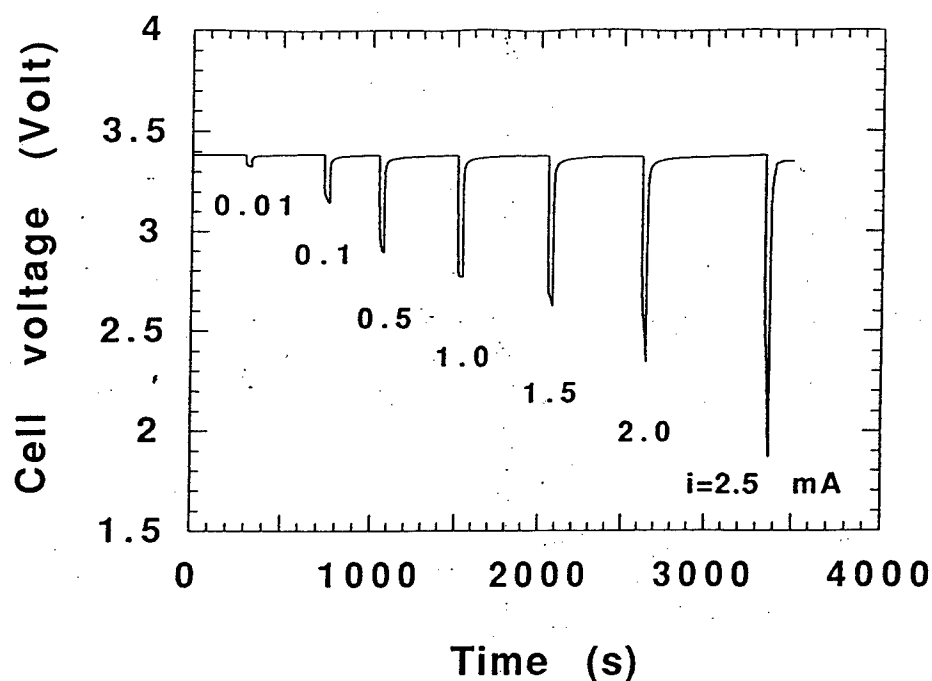


Figure 7- Pulse discharge at various current rates of the Li/Ag₂WO₄ thin-film, polymer battery at room temperature. Electrolyte: LiClO₄, PC/EC-PAN.

Conclusion.

The above reported preliminary results suggest that the battery is worth of consideration for a series of reasons. There are in essence:

i) the novelty of the electrodic reaction, which is different from the common intercalation processes and which has the unique advantage of providing flat and high discharge voltages and high rate capabilities. This electrode combination has been tested some years ago in our laboratory in liquid electrolyte cells (2,3) but never before in solid state cells.

ii) the exploitation of this novel electrodic combination for the fabrication of thin-layer, polymer, high performance and reliable lithium batteries which seems particularly suitable for the electronic market both in the consumer and in the military range.

Considering all these favourable aspects we will continue the study of this novel type of polymer batter by further testing its performance and by exploring alternative electroilyte or electrode structures .

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